SOME OF THE EFFECTS OF NATURAL GAS UPON THE PHYSICAL AND CHEMICAL PROPERTIES OF THE SOIL

by

RUSSELL STANLEY ADAMS, JR.

B. S., Kansas State University, 1958

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agronomy

KANSAS STATE UNIVERSITY
OF AGRICULTURE AND APPLIED SCIENCE

1959

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INTRODUCTION

Soils saturated with natural gas show severe physical, chemical, and biological changes. Soil aggregates are broken down and the soil frequently appears to be laminated or layered in structure. The color of the soil is lavender to dark black. Streaks of metallic red, and spots of black humic material may be observed in the subsurface horizons. The soil when disturbed has the odor of stagnant pond bottoms. Water will not penetrate it from above but seems to enter easily from the sides. Growth of vegetation on these areas may be accelerated, retarded, or completely absent. Microbial populations increase to such an extent that encrustations of living and dead colonies are readily visible.

Natural gas is very light and readily rises through the soil. Lateral penetration is dependent upon soil structure, but at most, does not extend more than a few feet beyond the gas leak. The area affected is so small that it is seldom an economic problem in agriculture and might even go unnoticed in fields of row crops. However, it does become a minor, but irritating source of damage suits to utility companies in towns and cities, because of damage to lawns and shrubbery.

After a preliminary examination of the problem, a questionnaire was sent to a number of gas and petroleum companies operating in various sections of the nation. Several companies representing a good cross-section of the United States, responded with useful and comprehensive evaluations of the problem in their

area.

A number of general statements could be drawn from their evaluations. First of all it was agreed that once the leaks are repaired, the detrimental effects upon plants eventually disappear. Several noted that damage to vegetation was most severe in arid areas. Finally, the commonly accepted method of reclamation is a thorough aeration of the soil in some manner, then reseeding and watering abundantly until vegetation is re-established.

This study was undertaken in an attempt to determine some of the physical and chemical effects of gas saturation of the soil. Emphasis was placed on those factors that might prove detrimental to plant growth.

REVIEW OF LITERATURE

Little research has been conducted with saturation of soils by natural gas because of the small areas affected. In 1930 Schollenberger (22) observed that oats germinated well on a gas-saturated soil but soon ceased to grow and died shortly afterwards. From a chemical examination he found a marked increase in exchangeable manganese with the element making up as much as 18 percent of the exchangeable cations. No ferrous iron was observed to be present. Martin[1] in 1953 concluded that the black material in the soil was the result of reducing action of

[1] Paper prepared by Dr. E. L. Martin, Chemistry Department, University of New Mexico, March 6, 1953 that was forwarded to the author in personal correspondence by Robert C. Heid, Assistant Leakage Detection Engineer, Columbia Gas System Service Corporation, Columbus, Ohio.

the gas. He reported the pH of the gas-saturated soil very alkaline, giving readings of 8.6 to 9.1. Martin discovered that by passing air through the dark-colored, gas-saturated soil he could get the soil to return to a normal color.

While studying "paraffine dirt" in 1952, Davis (8) discovered that he could produce this "paraffine dirt" by treatment of soils with natural gas. These soils became waxy in appearance and extremely hard when dried. Mass spectrometer analyses of soils collected from natural beds of "paraffine dirt" showed the presence of methane and ethane. The content of lipids was low, but the soil contained large amounts of reducing sugars. Davis reported the soil heavily saturated with yeasts, fungi, and bacteria and concluded that the microorganisms were converting the hydrocarbon gases into microbial cells. The build-up in organic matter and the waxy appearance of the soil were considered to be due to accumulation of these microbial cells.

Plice (18) reported similar effects with crude oil. He compared petroleum and natural gas with the comment that,

> Parallel effects of nitrogen fixation and organic matter formation occur in soils, in huge amounts around natural gas leaks. If soil is moist molds and bacteria rapidly attack the gas and the soil darkens in color within a week. The black material itself seems to be composed of microbial substances and 'carbonized gas' residue. It is high in humic material and nitrogen.

He found that petroleum-saturated soils would not wet from surface rainfall, but would wet only from the sides and below. Even from the sides, wetting was slow, but once wetted the soils remained so all summer. These spots when dried out

were found to be subject to serious wind erosion. Subsequent analysis disclosed a severe breakdown of aggregates and the soil had a silty feel to the touch. The redox potential also was lowered. A study of microorganisms disclosed an increase in numbers from 7.3 million to 110 million after a period of two years on these deeply oiled spots. The check during the same period increased from 8.1 million to 9 million.

In studying the microbial population of petroleum-saturated soils, Baldwin (2) observed that most types of bacteria were inhibited but that a few were greatly stimulated. No inhibitory effect was found upon molds.

That the accumulation of microbial cells may be responsible for the retarded wetting is indicated by the findings of Anderson and Byers (1). In studying the nature of organic colloids they found it almost impossible to wet all of the soil when it was impregnated with fungus cells at the rate of 9.1 percent.

A number of microorganisms are known to use methane as a substrate. Dworkin and Foster (10) reported that many organisms were capable of utilizing methane and ethane or ethane alone but they could find none capable of utilizing methane alone. However, Mycobacterium, Flavobacterium, Acremonium coccus, and Alcaligenes were listed as organisms capable of utilizing methane alone when other organic compounds were present in the substrate. Porter (19) reported that Methanomonas methanica, Pseudomonas aeruginosa, Bacterium aliphatium, and

Bacterium aliphaticum-liquefaciens were methane utilizers. Stone et al. (24) divided bacteria found in petroleum-saturated soils into three groups. The dominating group was Pseudomonas aeruginosa. The second group was not satisfactorily identified but they called it Achromobacter and considered it to be the same organism that is variously listed as Asperigillus sapolium and Pseudomonas. The third group they found present was Radiobacter or Alcaligenes radiobacter.

According to Egloff (11) natural gas is composed of methane, ethane, propane, and butane. Some natural gases contain traces of benzene and toluene. The better natural gas may be pure methane. Thus, natural gas is a suitable substrate for the previously mentioned organisms.

That microorganisms may be responsible for the conditions observed in gas-saturated soils is suggested by the work of several investigators. Hubbell and Gardner (12) considered that conditions that retard or upset the routine of microorganisms might affect soil structure adversely. In the absence of oxygen, such as occurs when natural gas displaces the oxygen from the soil atmosphere, vigorous microbial activity may result in an increase of substances in the reduced state, according to Broadbent (5). This is particularly true of iron and manganese. Waksman (26) believes iron utilizing bacteria may also utilize manganese compounds. He found many fungi and bacteria capable of oxidizing manganese carbonate to oxides of manganese, using cellulose and other carbohydrates for energy; also, the

manganese could be reduced to manganous forms. A major source of available iron, manganese, and sulfur to plants is due to the activities of microorganisms according to Clark (7). Unavailable forms are transformed to available by microbial oxidations and reductions.

MATERIALS AND METHODS

Description of Soil and Sites Used

Four field samples of gas-contaminated soils were collected. Two samples were selected at the sites of abandoned gas wells in Allen County, Kansas, near LaHarpe. The remaining two samples were collected at the sites of gas main leaks in the Manhattan community, Riley County, Kansas. All soils were silty clay loam in the surface horizon, becoming silty clay to clay in the lower profile. These soils will be referred to in the text according to the letters assigned to them at this point.

Soil A was collected at the site of an abandoned gas well in Allen County. Continuous gas seepage has been taking place at this spot for at least 25 years. The affected area is small (approximately six feet in diameter) but symptoms of gas saturation are severe. No vegetation occurs. This site is in a native pasture, and located in a slough.

Soil B was collected at the site of an abandoned gas well in Allen County. Gradual recovery of this spot has occurred over the past nine years. The barren area is now almost nonexistent, being no more than three feet in diameter. Some weeds

are now able to show limited growth even in the center of the area. This is in a cultivated field. Crops germinate; grow to about three or four inches in height; and become chlorotic and die.

Soil C was collected at the site of a gas main leak in Manhattan. When the leak was repaired in 1957 it had destroyed an area of lawn 15 by 25 feet. Vegetative growth is retarded at the present time.

Soil D was collected in Manhattan at the site of a slight gas main leak in progress. A small area of grass was killed and the growth of a spirea bush was retarded.

For laboratory treatments the surface six inches of a Cherokee silty clay loam was used.

Sampling Methods

In the analyses of field saturated soils, samples were taken from the center of the affected area with an appropriate tool for the tests involved. For chemical analyses a three-inch core of the profile was taken for soils A and B using an orchard auger. In order not to further damage the lawns a one-inch soil probe was used to collect samples from soils C and D. Check samples were taken on the perimeter described by a line located six feet from the area of visibly affected vegetation.

Experimental Procedure

Chemical Determinations. Determinations of total carbon, available phosphorus, and soil reaction were made. All soil samples for these analyses were air-dried; ground to pass through a 0.2-mm sieve; and thoroughly mixed. The pH of the soil was determined with a Beckman Zeromatic pH meter when the soil was at a moisture consistency of a thick paste. Available phosphorus was measured colorimetrically by Bray's sulfonic acid reduction method (13).

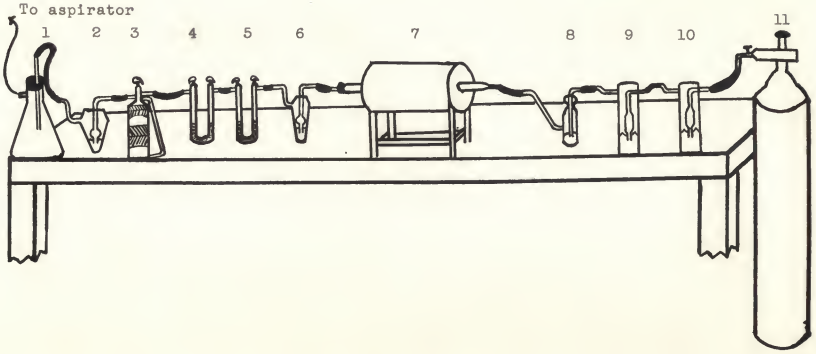
Total carbon was determined by the "Carbon Train" method. No attempt was made to remove chlorides or carbonates prior to analysis. It was feared some organic compounds, volatile or otherwise unstable in nature, that might exist in the soil as a result of chemical reaction with gaseous hydrocarbons would be lost. A diagram of the apparatus used is shown in Plate I. Two grams of air-dried soil plus two grams of cupric oxide were placed in an alundum boat. This boat was then placed into the furnace of the "carbon train," where it was held at a temperature of 925 to 930° C. for a period of 30 minutes. The silicon tubes were found to break easily from thermal shock if cold alundum boats were placed in the furnace while it was still hot. In order to maintain continuous use of the apparatus and to eliminate the breakage of these tubes without cooling the furnace, the alundum boats were kept warm and dry over a Bunsen burner. Soil samples were transferred to the boats with tongs and asbestos gloves. Then the boat was allowed to come to an

EXPLANATION OF PLATE I

A diagram of apparatus used in the "carbon train" for determination of total carbon.

1. Aspirator flask
2. Bubble counter
3. Absorption bottle
4. $Mg(ClO_4)_2$ trap
5. 40-mesh Zn trap
6. H_2SO_4 scrubber
7. Furnace
8. Mercury valve
9. 10% KOH scrubber
10. 10% KOH scrubber
11. Bottle of oxygen

PLATE I



equilibrium temperature just at the mouth of the furnace, 200 to 250° C. before final insertion to the center of the heating unit.

A stream of purified oxygen was passed over the boat in the furnace at a rate just sufficient to enable a distinct count of bubbles as they passed through the bubble counter (approximately 1100 to 1500 ml. of oxygen in 30 minutes). The oxygen was purified by passing through two 10 percent KOH scrubbers. The gas resulting from this oxidation was passed through a sulfuric acid scrubber, a 40-mesh zinc trap, and a $Mg(ClO_4)_2$ trap in order to remove water vapor and chlorine, nitrogen, and sulfur dioxide gases. The CO_2 and oxygen remaining were then passed through an absorption bottle containing alternate layers of glass wool, ascarite (a sodium hydrate asbestos), and $Mg(ClO_4)_2$. The ascarite to absorb the CO_2 and the $Mg(ClO_4)_2$ to absorb any water, formed by the reaction of CO_2 with the ascarite. The increase in weight of the absorbants was considered to be the amount of CO_2 formed by the oxidation of the carbon in the soil.

Soil samples A, B, and D were analyzed for exchangeable ferrous iron and manganous manganese according to procedures described by Jackson (13). For these analyses, fresh samples were taken with a soil probe and determined as rapidly as possible after collection.

Using a Fischer titrimeter, pH titration curves were determined for soil samples A and B. Ten-gram samples of soil

were diluted with 40 grams of water. Two samples of each soil were titrated, one with 0.1 N NaOH and one with 0.1 N HCl. Titration proceeded by adding five ml. of acid or base and then determining the pH of the solution and continued until the pH of the titrated solution approached that of the titrant.

Exchangeable ferric iron was measured in soils A and B following the procedure outlined by Jackson (13). For these analyses air-dried soil, ground to pass through a 0.2-mm. sieve was used.

Oxidation potentials were measured in the soil by use of a Portable Precision Potentiometer. A neutral platinum electrode and a silver, silver chloride reference electrode were used. Measurements were made in the field when the soil was allowed to come to an equilibrium until a constant reading was obtained.

Physical Determinations. In order to collect data for moisture tension curves the water holding capacity of soils A and B was determined at various tensions. Soil was air dried and ground to pass through a 0.2-mm sieve before treatment. Upon discovery that fresh, unground soil in the gas-saturated samples had a higher water retention than the air-dried soil, the procedure was repeated for the 0- to 6-inch layer using fresh, unground soil material from soils A and B. Soil samples were placed in rubber rings on the tension apparatus and allowed to equilibrate with water for 48 hours. A period less than this would not completely saturate the gas-impregnated soils. The

water retention of each soil was determined at 0, 200 mm., 1/3 atm., 400 mm., 600 mm., 1 atm., and 15 atm. water tension. Each tension was applied to respective samples for a period of 24 hours. The soil samples were weighed, oven dried at 105° C. for 24 hours, and the dried soil reweighed. The weight lost in drying was divided by the weight of the dry soil to determine the water retention of the sample at the tension studied. For tensions of one atmosphere or less a porous plate apparatus was used. For higher tensions it was necessary to employ a pressure membrane apparatus.

Pore capacities and bulk densities were studied at sites A and B. Three-inch cores were taken at each of these sites and their checks with a Uhland Soil Sampler. Sampling was made when soil was at field capacity. When it was discovered that water would not saturate the gas-impregnated soils by ordinary processes they were placed in water in a vacuum desiccator for 24 hours. The water used to saturate these soils contained 30 ppm. of Dowcide B[1] to eliminate microbial activity. Saturated samples were removed from the desiccator, weighed and placed on a porous plate apparatus under a water tension of 10 inches until they reached constant weight number 1. This loss in weight was reported as comprising the macropores in the soil. The cores were then oven dried at 105° C. until constant weight number 2 was attained. This loss in weight was reported as micropore

[1] Eighty-five percent sodium trichlorophenate, 15 percent inert, a product of the Dow Chemical Co.

space. Percent pore space was calculated by dividing the pore space by the internal volume of the core. The metal cores were thoroughly cleaned, oven dried, and weighed. Constant weight number 2 less the weight of the core was reported as the weight of soil per core. The bulk density was computed by dividing the weight of the soil by the volume of the core.

Greenhouse Experiments and Laboratory Saturation with Natural Gas. Soil from sites A and B was brought into the greenhouse. Two pots of soil from each site and two pots from each adjacent normal soil were planted to Cherokee oats. Germination and growth were observed for two months.

Six three-inch cores were taken with a Uhland Soil Sampler at site A. These cores were taken into the greenhouse and wheat was planted on the surface of each core. All cores were watered on the surface until wheat had germinated and reached an inch in height. Then in an effort to determine whether osmosis would carry water to the plant fast enough to maintain growth, three cores were watered from the bottom and three were watered from the top. Growth of wheat was observed for two months.

Six pots of Hong-kong soybeans were established on Cherokee silty clay loam. To determine if the water soluble extracts contained any toxic materials three pots were watered with water extracts from the gas-impregnated soils and three pots were watered with tap water. Water soluble extracts were leached from fresh soil samples by refluxing in a Soxhlet Extractor with

distilled water for a period of 24 hours. Growth was observed for three weeks.

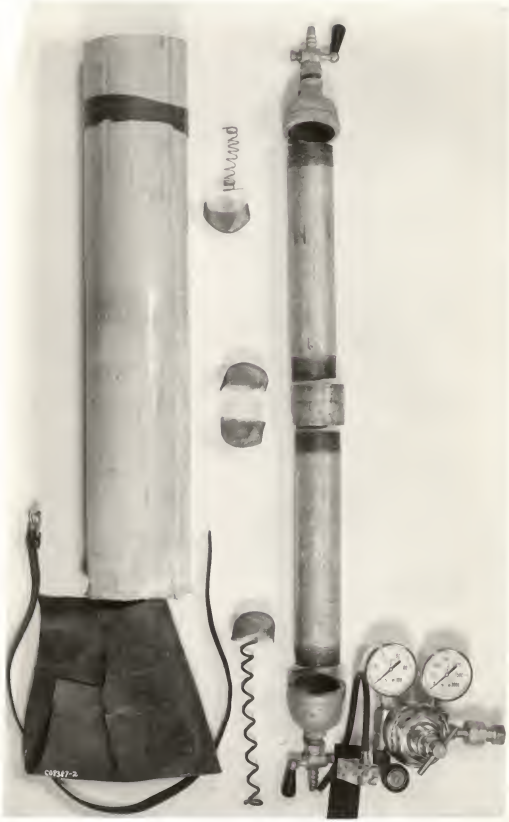
One thousand-gram samples of Cherokee silty clay loam were saturated with natural gas by use of the apparatus pictured in Plates II and III. This apparatus consisted of two one-foot sections of two-inch galvanized gas pipe connected by a collar. A reducer at each end was connected to a gas cock. Air spaces were provided internally between layers of soil with the purpose of allowing gas pockets to form and to enable separation of the two sections without disturbing the soil. These pockets were made with domes of screen wire. The wire domes were held in place at each end with heavy wire coils. The flow of gas into the soil was controlled by a Matheson gas flowmeter. Gas passed through the soil and out of the hood exhaust. When saturating at -1° C. a jacket consisting of a six-inch galvanized metal pipe was fitted over the gas pipe. A rubber cap was fitted over the bottom of the gas pipe and jacket and sealed to make water tight. The jacket was then filled with ice and NaCl to maintain a constant temperature of -1° C.

Soil samples were saturated with gas in a series of four treatments. Series one comprised of saturation of samples at room temperature under 24 hours continuous saturation. Gas cocks were closed while gas was still passing through the system and was allowed to stand seven days before analysis for an increase in carbon. Series two consisted of saturation of soils continuously at -1° C. for a period of 24 hours. The apparatus

EXPLANATION OF PLATE II

The unassembled apparatus used to saturate soils with natural gas. The assembly at left was used as a jacket around the assembly at right to contain ice, sodium chloride, and water.

PLATE II



EXPLANATION OF PLATE III

The assembled apparatus used to saturate soils with natural gas in the laboratory, without the water jacket used to maintain cold temperatures.

PLATE III

was then placed in a cold room and held at $0^{\circ} \pm 1^{\circ}$ C. for seven days prior to analysis for an increase in carbon. In series three, samples were saturated continuously for 48 hours at -1° C. and then placed in a cold room at $0^{\circ} \pm 1^{\circ}$ C. for 27 days before analysis. Series four was saturated for 48 hours, using 8-hour periods over a 6-day span. When not under saturation, samples were held in a cold room. Upon completion of saturation the samples were held in a cold room at $0^{\circ} \pm 1^{\circ}$ C. for 20 days before analysis. All samples to be saturated when cold were placed in the cold room at least seven days prior to saturation. All samples were at a moisture level of field capacity. For all saturations the flowmeter was adjusted to 0.008 cubic feet per hour. At this rate 1.9 cubic feet of gas passed through the soil in 24 hours.

DISCUSSION AND RESULTS

Initially an attempt was made to determine whether organisms present in the gas-saturated soil were those known to utilize lower hydrocarbon gases as a substrate. Cultures were prepared and examined by a technician in the Department of Botany. Three genera were isolated. These included Aspergillus, Penicillium, and Mycobacterium. Only two species were identified: Asperigillus flavius and Asperigillus niger. The genus Asperigillus was most abundant of those isolated and Asperigillus flavius organisms comprised almost all of these. Dworkin and Foster (10) reported Mycobacterium among the organisms capable

of utilizing methane in the presence of other carbonaceous material. Stone et al. (25) suggested that a species of Asperigillus might be the same organisms as their Achromobacter found in petroleum-saturated soils.

At all of the sites studied, the gas-impregnated soil contained more carbon than the normal soil beside it, Table 1. This increase was most pronounced in the surface foot of soil. Total carbon was almost three times as great as that in the normal soil throughout the profile at site A. At three sites studied there was general increase in pH and available phosphorus, Table 1. Only in the surface six inches was this not true. A possible explanation for this is the great accumulation of organic matter in the surface layer. Decay of this organic matter could increase the CO_2 content of the surface layer and depress the pH and available phosphorus. The pH of the surface of the normal soil at site B is higher than the rest of the profile because of recent lime applications.

Only site D showed a depression of pH and available phosphorus in the gas-saturated soil. The normal soil here was slightly alkaline. This may indicate that the products of gas saturation tend to buffer the soil toward neutrality or pH 7 rather than make the pH more basic. The lawn at this site had been heavily fertilized with phosphatic fertilizers, while the row of shrubbery where the gas leak was located had not been fertilized. This was apparent in the surface six inches and may

Table 1. A comparison of total carbon, available phosphorus, and pH between normal and gas-saturated soils at four sites.

Site	Depth inches	Total carbon		Available phosphorus		pH	
		Gas	Normal	Gas	Normal	Gas	Normal
		%		ppm.			
A	0- 6	7.16	2.62	6.0	6.0	5.6	7.0
	6-12	5.31	2.10	13.0	2.5	7.0	6.8
	12-18	4.75	1.94	12.0	2.5	7.1	6.9
	18-24	3.56	1.33	10.0	1.0	7.2	7.2
	24-30	3.45	1.13	11.5	3.0	7.3	7.4
B	0- 6	2.98	1.56	12.5	13.5	6.8	6.8
	6-12	2.48	1.10	10.5	5.5	7.2	5.9
	12-18	1.95	1.05	11.5	4.0	7.3	5.8
	18-24	1.05	0.87	8.0	4.0	7.3	6.2
	24-30	0.71	0.60	5.5	5.5	7.0	6.7
	30-36	0.57	0.56	7.0	4.5	7.0	7.1
C	0- 6	3.24	2.41	9.0	12.5	7.0	6.7
	6-12	2.25	1.83	9.0	6.0	6.8	6.3
	12-18	1.76	1.66	6.3	8.0	6.3	6.0
	18-24	1.33	1.30	6.0	3.5	6.0	5.8
	24-30	0.83	0.60	6.3	4.0	6.0	5.9
	30-36	0.68	0.56	3.8	2.3	6.3	6.0
D	0- 6	6.32	2.36	10.0	47.5	7.3	7.6
	6-12	3.29	2.07	33.0	27.0	7.6	7.7
	12-18	2.49	1.80	24.0	35.0	7.4	7.5
	18-24	2.08	1.51	24.0	31.0	7.1	7.3
	24-30	1.63	1.38	18.0	25.0	7.1	7.2
	30-36	1.50	1.16	17.5	20.0	7.1	7.2

have influenced the amount of available phosphorus throughout the profile in the normal soil.

Plice (18) pointed out that petroleum-saturated soil would not wet but once wet, remained that way. Carr (6) questioned the ability of the plant to remove enough water from the petroleum-saturated soils to water itself. Schollenberger (22) noticed that the gas-saturated soils contained more water, but

attributed this to the lack of vegetation. Gas companies reported that damage to plant growth on gas-saturated soils was more noticeable in arid areas. From the work of previous investigators and the report of the gas companies it was felt that gas-impregnated soils might have a higher moisture retention. Sites A and B were chosen for this analysis as it was felt this phenomenon, if present, should be more pronounced on the more severely affected soils. In the 0- to 6-inch layer of soil A the water retention of the gas-impregnated soil was increased markedly over the normal soil. The fresh, unground soil contained 43 percent moisture at the wilting point, Table 2. This is 27 percent more water than the normal soil was capable of retaining and well above the 36 percent field capacity of the normal soil. The field capacity of the gas-impregnated soil, however, was 71 percent. There would be 26 percent available water between field capacity and wilting as opposed to 18 percent in the normal soils. The fresh, unground soil gave markedly higher results in soil A, but there was little difference in soil B. The greater water retention of the gas-saturated soils, though still apparent, fell off in the 6- to 12-inch layer at site A. At site B the gas-impregnated 0- to 6-inch layer contained only two percent more water at field capacity and only four percent more water at the wilting point. In the 6- to 12-inch layer, differences were almost non-existent. Note Plates IV, V, VI, and VII for the water retention curves of these soils.

Table 2. A comparison of water retention at field capacity and wilting point between gas-saturated and normal soils.

Site	Depth inches	Retention field capacity		Retention wilting point	
		Gas	Normal	Gas	Normal
		%			
A	0- 6	71*	36	43*	18
	6-12	52	39	25	23
B	0- 6	31*	29	15*	11
	6-12	39	38	19	19

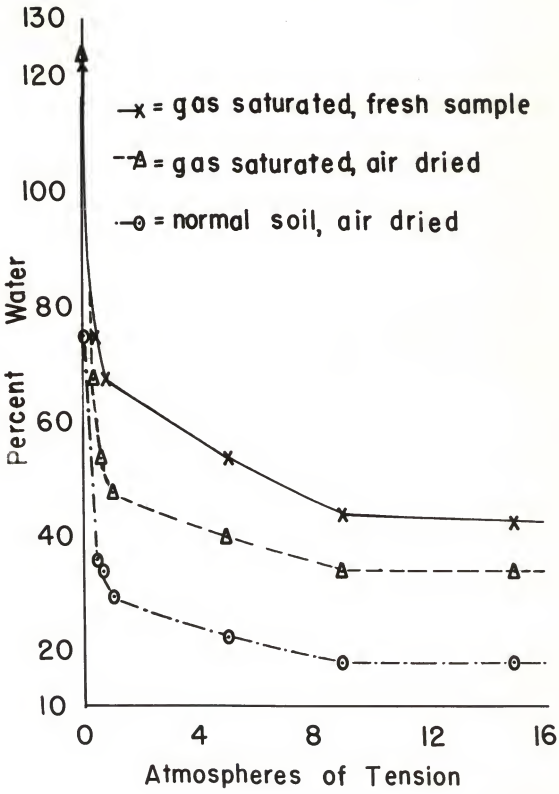
* Fresh, unground samples used.

The study of ferrous and manganous ions disclosed a marked increase in manganous manganese at all sites, Table 3. Sites A and B contained almost no exchangeable manganese in the normal soils. In the gas-impregnated soils, exchangeable manganese was as high as 64 ppm. at site A. In general, ferrous iron was increased. At sites B and D the increase was small, but at site A the increase was pronounced. Schollenberger (22) reported no ferrous iron present in his tests. He did not, however, make analyses on fresh soil samples. His samples had been stored in the laboratory for some time before analysis. It was observed that in these analyses unless samples were analyzed within 14 days of sampling no ferrous iron would be found. Results were not satisfactory when soil had been in the laboratory more than seven days even when stored in tight moisture cans. Originally site A had been sampled March 2, 1959. Ferrous iron determinations on site A were the last determinations at that time and results were not good, but indicated that ferrous iron was

EXPLANATION OF PLATE IV

The water-retention curves for fresh unground samples of gas-saturated soil, for air-dried samples of gas-saturated soil, and for air-dried samples of normal soil of the 0- to 6-inch layer at site A.

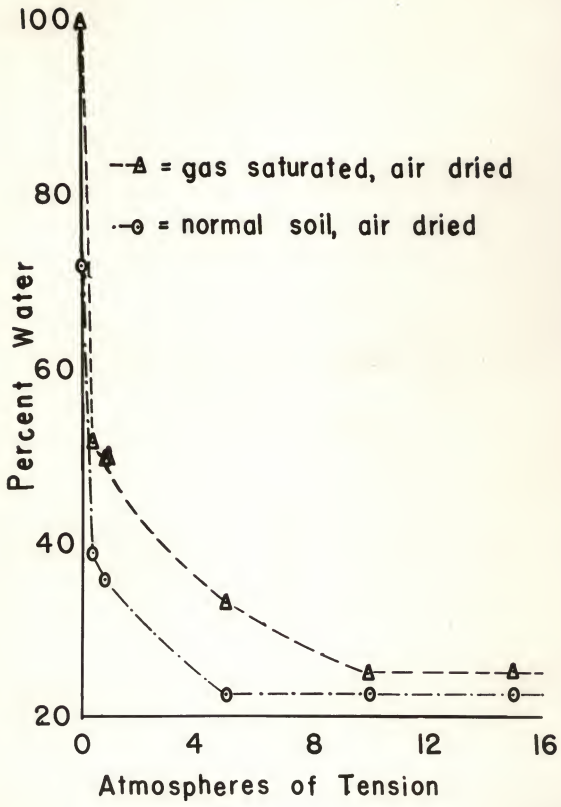
PLATE IV


130
120
100
80
60
40
20
10
Percent Water
—x = gas saturated, fresh sample
--Δ = gas saturated, air dried
·—o = normal soil, air dried
0
4
8
12
16
Atmospheres of Tension

EXPLANATION OF PLATE V

The water-retention curves for air-dried samples of gas-saturated and normal soils of the 6- to 12-inch layer at site A.

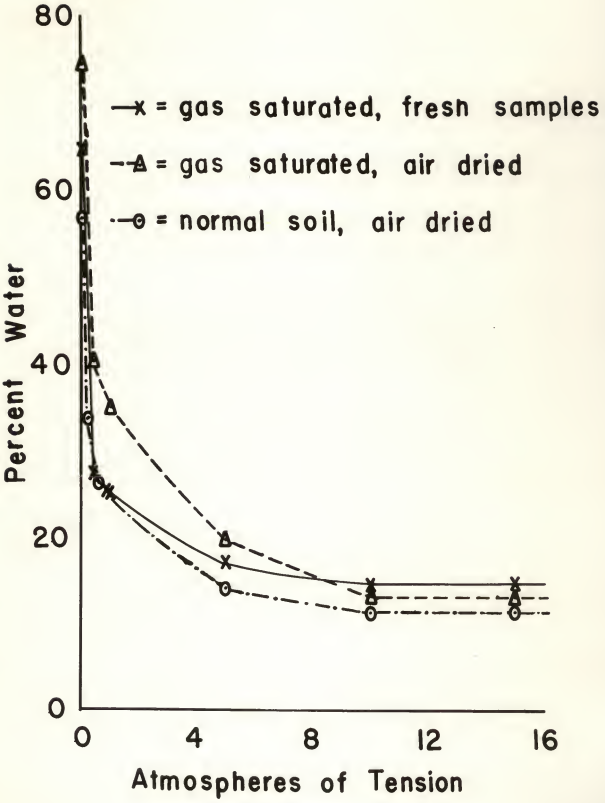
PLATE V


100
80
60
40
20
Percent Water
--Δ = gas saturated, air dried
·-o = normal soil, air dried
0
4
8
12
16
Atmospheres of Tension

EXPLANATION OF PLATE VI

The water-retention curves for fresh unground samples of gas-saturated soil, for air-dried samples of gas-saturated soil, and for air-dried samples of normal soil of the 0- to 6-inch layer at site B.

PLATE VI


80
60
40
20
0
Percent Water
—x = gas saturated, fresh samples
--Δ = gas saturated, air dried
·-·o = normal soil, air dried
0
4
8
12
16
Atmospheres of Tension

EXPLANATION OF PLATE VII

The water-retention curves for air-dried samples of gas-saturated and normal soils of the 6- to 12-inch layer at site B.

PLATE VII

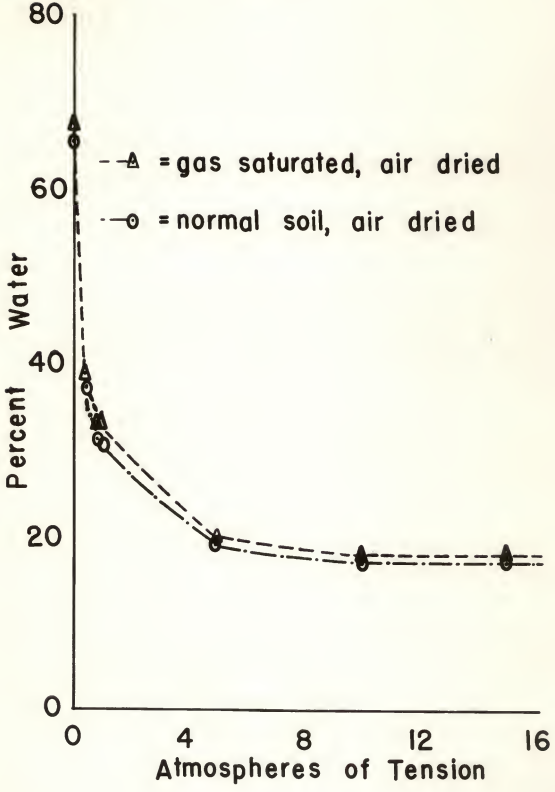

80
60
40
20
0
Percent Water
= gas saturated, air dried
= normal soil, air dried
0
4
8
12
16
Atmospheres of Tension

Table 3. A comparison of exchangeable manganous and ferrous ions between normal and gas-saturated soils at sites A, B, and D.

Site	Depth inches	Exchangeable Mn^{++} ppm		Exchangeable Fe^{++} ppm		Fe^{++}/Mn^{++}	
		Gas	Normal	Gas	Normal	Gas	Normal
A[1]	0- 6	4.96	0	77.21	18.43	15.8	--
	6-12	11.18	0	151.40	24.23	13.6	--
	12-18	10.22	0	119.10	23.02	11.6	--
	18-24	30.34	0	119.55	19.51	3.8	--
	24-30	55.52	0	116.60	26.32	2.1	--
	30-36	63.63	1.17	111.60	26.50	1.7	22.7
B[2]	0- 6	0.59	trace	20.09	15.83	34.1	--
	6-12	3.42	trace	17.36	16.60	5.1	--
	12-18	7.14	trace	30.78	25.56	4.3	--
	18-24	20.58	trace	38.76	16.37	1.8	--
	24-30	24.84	trace	35.10	16.92	1.4	--
	30-36	25.83	0.74	33.32	25.09	1.2	34.9
D[3]	0- 6	7.87	1.36	29.29	24.57	3.7	18.2
	6-12	13.86	0.73	37.53	17.85	2.7	24.5
	12-18	19.43	1.38	53.19	27.26	2.7	19.8
	18-24	15.49	1.32	31.82	41.84	2.1	31.7
	24-30	15.43	1.19	52.74	37.47	3.4	31.5
	30-36	4.85	0.82	51.68	32.73	10.7	40.0

[1] Soil for the Mn^{++} determinations was taken March 2, 1959 and soil for Fe^{++} determinations was taken April 6, 1959.

[2] For determinations at site B, soil samples were collected March 2, 1959.

[3] For determinations at site D, soil samples were collected February 16, 1959.

increased in the gas-saturated soils to about the same extent as in sites B and D. One month later a marked increase in ferrous iron was found in the gas-saturated soils at site A. This suggests that the difference in manganous manganese and ferrous iron may even be greater during the growing season when

microorganisms are active.

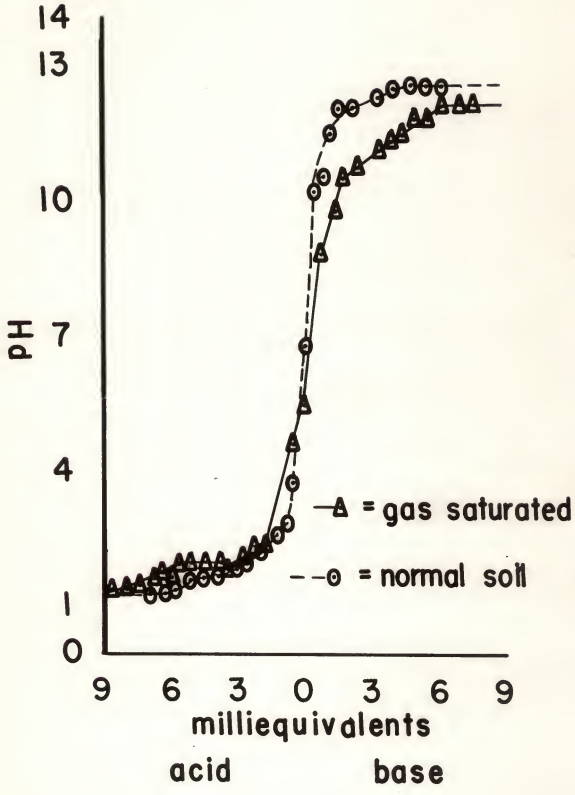
The pH-titration curves determined for sites A and B show a definite inflection at pH 2 in the gas-saturated soils, Plates VIII, IX, X, and XI. Two pH-titration curves were determined in both the normal and the gas-saturated soils at these sites, one curve in the 0-6 inch layer and one curve from the 6-12 inch layer. The 6-12 inch layer gave the sharpest inflection in the pH-titration curves. Subsequent determination of ferric iron verified a marked increase in ferric iron in gas-saturated over the normal soils, Table 4. This increase was least pronounced in the surface layer. A large accumulation in the 6- to 12-inch layer indicated that ferric iron leached rapidly from the 0- to 6-inch layer but then slowed in its downward progress. This is apparent at site B where the 12- to 18-inch layer contained the most ferric iron. Each preceding layer thereafter was reduced in ferric iron content. At site A, however, the quantity of ferric iron was reduced in the 12- to 18-inch layer. At greater depths in the profile the ferric iron increased progressively. Ferric iron in the gas-saturated soils was increased over the normal soils from 1.5 to 17 times. Air-dried soil was used in these analyses and the values reported include the ferrous iron originally present.

Waterlogged soils are known to be in a reduced condition. The high water retention and the high manganous ion content of the gas-saturated soils suggested that they might be in a reduced state. Measurements of oxidation potentials verified

EXPLANATION OF PLATE VIII

The pH-titration curves of the normal and gas-saturated soils of the 0- to 6-inch layer at site A.

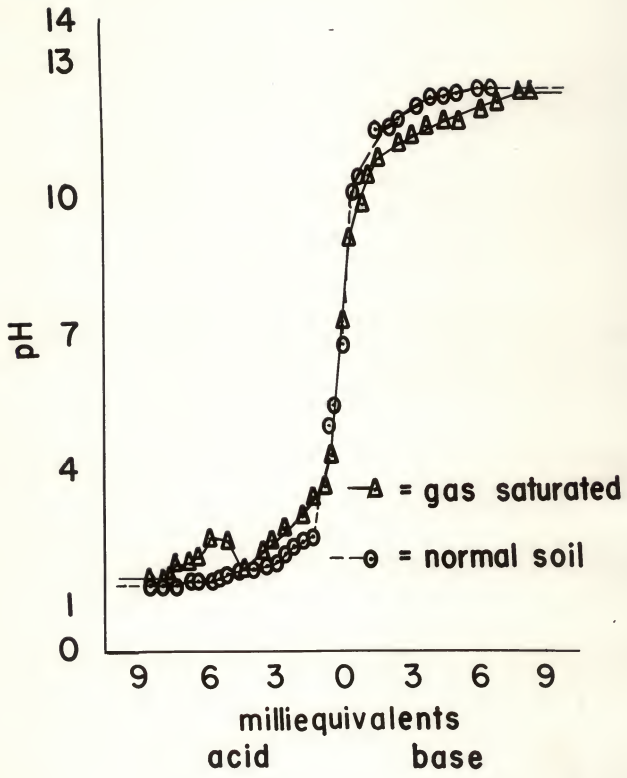
PLATE VIII


14
13
10
pH 7
4
1
0
9 6 3 0 3 6 9
milliequivalents
acid
base
—Δ = gas saturated
– –o = normal soil

EXPLANATION OF PLATE IX

The pH-titration curves of the normal and gas-saturated soils of the 6- to 12-inch layer at site A.

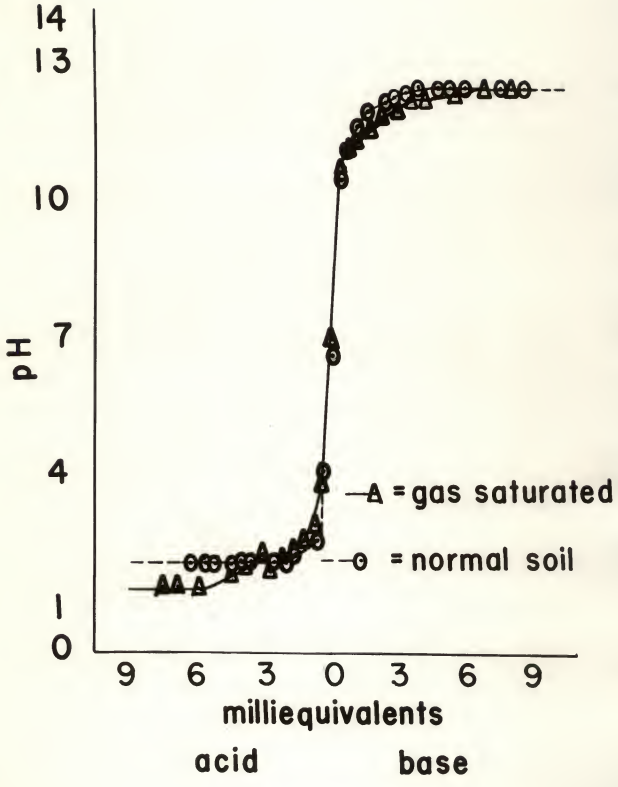
PLATE IX


14
13
10
7
4
1
0
pH
9 6 3 0 3 6 9
milliequivalents
acid
base
= gas saturated
= normal soil

EXPLANATION OF PLATE X

The pH-titration curves of the normal and gas-saturated soils of the 0- to 6-inch layer at site B.

PLATE X


14
13
10
7
4
1
0
pH
9 6 3 0 3 6 9
milliequivalents
acid
base
A = gas saturated
o = normal soil

EXPLANATION OF PLATE XI

The pH-titration curves of the normal and gas-saturated soils of the 6- to 12-inch layer at site B.

PLATE XI

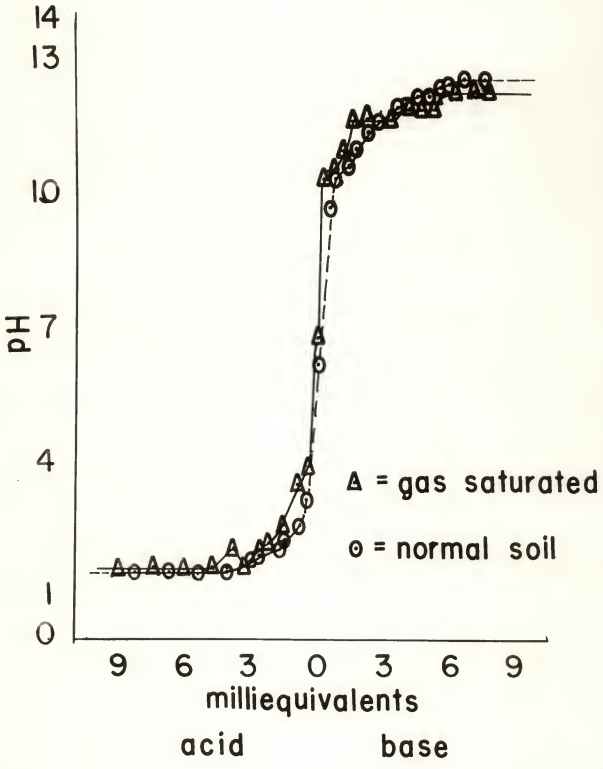

14
13
10
pH 7
4
1
0
9 6 3 0 3 6 9
milliequivalents
acid
base
Δ = gas saturated
o = normal soil

Table 4. Comparison of exchangeable ferric iron in gas-saturated and normal soils at sites A and B.

Depth inches	Site A		Site B	
	Gas	Normal	Gas	Normal
	ppm.			
0- 6	820	130	275	160
6-12	2,140	130	1,550	170
12-18	1,670	130	1,780	180
18-24	1,890	170	700	130
24-30	2,250	130	570	160
30-36	--	--	350	200

this, Table 5.

Table 5. Oxidation potentials of the gas-impregnated and corresponding normal soils.

Site	Gas-saturated soil	Normal soil
	mv.	
A	687	-913
B	982	-833
D	897	-368

The potentials in Table 5 are a measure of the capacity of the soil to undergo oxidation. Those with a negative potential are well oxidized and have little tendency to undergo further oxidation. The gas-saturated soils are reduced and have a large potential for oxidative processes.

Results in the porosity and bulk density studies were similar to those obtained in the water retention studies. Site A had a marked change in porosity and bulk density with much less change at site B. The two surface layers were studied in these determinations. At site A the bulk density of the gas-saturated soil

was greatly reduced with the surface soil being less than one (0.74), Table 6. This corresponds to the 125 percent moisture at zero tension in the water retention studies. Only a soil with a bulk density less than one could have a water-holding capacity this high at saturation. The 6- to 12-inch gas-saturated layer at site A had a bulk density of 1.06, much less than the 1.35 bulk density of the normal soil. Total porosity was greater in the gas-impregnated soils. Most of this increase was in the micropores, Table 6. At site B there was a slight decrease in bulk density with little change in porosity.

Even though samples were taken at field capacity the gas-saturated soils were observed to expand considerably during saturation with water. This expansion occurred under vacuum wetting. When oven dried these same samples were observed to shrink much more than the normal soils. Attempts to re-wet the oven-dried cores of gas-impregnated soils, even under vacuum wetting, were unsuccessful.

It was found in the greenhouse experiments that merely transferring the gas-saturated soil seemed to eliminate its detrimental influence on the growth of vegetation. Over the two-month period that the oats were studied there was no observable difference between the plants grown in pots of gas-saturated and normal soils. It is now felt that the stirring and air drying of the soil resulted in oxidation of the excessive manganous ion. No difference was observed in the soybeans watered with water extracts, extracted from gas-saturated soils,

Table 6. Comparison of bulk densities and porosities between the gas-saturated and the normal soils at sites A and B.

Site	Depth inches	Total porosity		Macropores		Macropores	
		Gas	Normal	Gas	Normal	Gas	Normal
		%		cc.		%	
A	0- 6	70.36*	55.06	24.6	31.5	7.03	8.10
A	6-12	64.28	55.45	37.9	23.0	10.83	6.57
B	0- 6	55.13	53.83	28.9	21.0	8.26	6.00
B	6-12	53.67	54.83	41.6	33.0	11.88	9.43

		Micropores		Micropores		Bulk density	
		Gas	Normal	Gas	Normal	Gas	Normal
		cc.		%		g./cc.	
A	0- 6	221.3	164.4	63.33	46.96	0.7392	1.3526
A	6-12	187.1	166.1	53.45	48.88	1.0552	1.3496
B	0- 6	164.1	167.4	46.87	47.83	1.2482	1.2887
B	6-12	146.4	158.9	41.81	45.40	1.3235	1.3964

* The metal cores used in these determinations had an internal volume of 350 cc.

and tap water. All plants were normal at the end of the period.

Some difference was observed in the methods of watering the wheat plants. From the fifth to the seventh week those plants watered from the bottom appeared to yellow. During the seventh and eighth week this yellowing disappeared and all plants appeared normal. At the end of the eighth week the roots had penetrated almost to the bottom of the core. Apparently the roots had difficulty in acquiring enough water about the fourth week, but by the seventh week had grown near enough to what might be considered the effective water table that they had no difficulty in getting needed water. Had six-inch cores been taken, more pronounced results might have been obtained.

Through saturation of the soil with natural gas in the laboratory it was hoped to determine if the methane was fixed directly to the soil causing an increase in carbon content. According to Russell (21) dry clays absorb permanent gases at room temperature and the amount they absorb is in proportion to the gas pressure and increases as the critical temperature increases. He pointed out that gases are readily displaced by water vapor or water, and that in fact this displacement of absorbed gases is an important mechanism in the observed break-up of dry soil clods when they are wetted. Weiser (27) expressed de Saussure's hypothesis that the absorbed gas or vapor forms a thick compressed polymolecular film around the absorbent particle, but this suggests a polarized molecule. It seems unlikely this effect could be obtained with the methane molecule.

Analysis of series 1, the treatment at room temperature, disclosed no increase in carbon, Table 7. This, however, does not mean that the gas could not be trapped in pores in the soil and remain there for long periods. This means only that no methane was fixed which was stable enough to be held by the clay until it could undergo oxidation in the "carbon train."

Table 7. Carbon fixed by soil saturated with natural gas in the laboratory.

Sample	Total carbon	Increase in carbon	Carbon after two weeks
		%	
Control	1.28	--	--
Series 1	1.24	0	--
Series 2	1.63	0.35	1.30
Series 3	1.60	0.32	1.27
Series 4	1.55	0.27	1.29

One other possibility remained. If gas could form a hydrate it would explain one possible source of the deflocculation of the soil and a possible means of fixation. According to Dotterweich (9) lower hydrocarbon hydrates are a source of trouble to pipeline companies. When high pressure gas is allowed to expand, it decreases in temperature and hydrates. Leaks in high pressure gas lines would cause similar conditions. Parent (16) concluded that all lower hydrocarbon gases formed hydrates capable of existing up to 60° F. Temperatures must be low to form but none could react with ice. He proposed seven waters of hydration for methane and eight waters of hydration for ethane. Roberts et al. (20) found both methane and ethane

with seven moles of water of hydration. They considered the crystal structure of the hydrate to be determined by the lattice structure of ice. They reported isomorphism occurring readily. Series two, three, and four were saturated at -1° C. in an effort to produce the methane hydrate in the soil. All were successful in fixing roughly 0.003 gram of carbon per gram of soil. None of the fixed carbon was stable, however, as it had disappeared within two weeks after being brought to room temperature. Time and quantity appeared to be no factor in the amount of gas fixed.

Hydrates of methane and ethane could be a ready substrate for microorganisms resuming their activities in the soil in the spring. In the slowly warming soil such hydrates could persist for considerable time. However, these microorganisms must be able to use the natural gas directly in the soil as the conditions observed in gas-saturated soils are found where no frost occurs.[1]

It is felt that this series of tests suggests that the natural gas is not permanently fixed to the clay colloid. The increase in carbon must be due to the activities of microorganisms using the natural gas directly as a substrate.

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[1] Personal correspondence with H. D. Levene, Research Engineer, El Paso Natural Gas Company, El Paso, Texas.

SUMMARY AND CONCLUSIONS

Comparison of gas-saturated soils and adjacent normal soils revealed a large increase in total carbon. With the exception of one site, site D, phosphorus and soil reaction also increased. Heavy fertilization of the adjacent soil may account for the increase in phosphorus at this site. Site D was the only site where the normal soil was slightly alkaline in nature. The decrease in pH of the gas-saturated soil at this site may indicate a buffering substance in the gas-impregnated soils rather than a tendency for the pH to increase.

Water retention of the soil at site A was much higher in the gas-saturated soil, but at site B retention was only slightly greater than in the normal soil. This increase was reflected at both the field capacity and the wilting point levels. There was more water available to the plant between these levels in the gas-impregnated soils. This then does not seem to be a source of plant injury. Such an increase in moisture could make a more suitable microclimate for microorganisms and maintain higher water levels which could influence the reducing conditions found present in the gas-saturated soils.

The gas-saturated soils were found to be in a reduced condition. According to Bear (3) this should increase reduced iron and manganese. Analyses of these soils proved this to be true with a marked increase in manganous manganese. This increase in manganous and ferrous ions may be, in part, responsible for the pH increase at sites A, B, and C as manganous and ferrous

ions tend to be basic (Peters, 17). Both Bear (3) and Somers and Shive (24) stated that ferrous iron oxidizes easily and if a strong oxidizing agent such as manganese is present, it may be completely oxidized. Under these conditions little ferrous iron would be expected in a soil high in manganous ion unless it was being constantly replenished from some source. That this may be true is indicated by the increase of exchangeable ferric iron in the gas-impregnated soils. Russell (21) reported the dioxide of the hydrated oxide $Mn_2O_3 \cdot H_2O$ as the form manganese would probably take in the soil. With manganese in this form and microorganisms continuously reducing iron to the ferrous form, conditions would be right for a buildup of both manganous and ferric ions in the soil.

$$Mn^{+++} + Fe^{++} \longrightarrow Mn^{++} + Fe^{+++}$$

Somers and Shive (24) stated that pathological symptoms in the plant are the same for either an excess of ferrous iron or a deficiency of ferrous iron due to an excess of manganous manganese. They consider a ratio of Fe^{++}/Mn^{++} of 2/1 as most ideal for plant growth. Somers et al. (23) and Bear (3) consider 1.5/1 to 2.5/1 as the most favorable Fe^{++}/Mn^{++} ratio. Under these circumstances the Fe^{++}/Mn^{++} ratio in the gas-impregnated soils might be even more favorable than the normal soils. The Fe^{++}/Mn^{++} ratios determined in this investigation more nearly fit this optimum in the gas-impregnated soils. Olson and Carlson (15) found ratios of Mn^{++}/Fe^{++} of 1/1 to 13/1 in sorghum plots with no appearance of chlorosis.

However, Black (4) reported as little as four ppm. of manganese would depress the yields of lespedeza, soybeans, and barley. Corn did not show any intolerance until 15 ppm. of manganous manganese ion was present in the soil. Morris and Pierre (14) found that 1 to 10 ppm. of manganous ion damaged five legume stands they were studying. If the quantity of manganous manganese is more important on some crops than the Fe^{++}/Mn^{++} ratio, the gas-impregnated soils could be injurious to crops. All of the sites studied contained more manganous ion in some part of the profile than the maximum 15 ppm. stated above.

None of the gas-impregnated soils transferred to the greenhouse produced any injury to plants grown on them. This was considered due to the drying and aeration the soil received in transfer.

Soils saturated with natural gas in the laboratory were not found to increase in carbon content except when the soil was saturated at -1° C. Such conditions would be suitable for the formation of the methane and ethane hydrates. When returned to room temperature the carbon content of the soils rapidly returned to that of the control.

ACKNOWLEDGMENT

The author wishes to express his appreciation to the Agronomy Department Staff of Kansas State University for its helpful advice and interest. Special appreciation is expressed by the author to his major instructor Dr. Roscoe Ellis, Jr.

Appreciation is also expressed to persons other than those on the Agronomy Staff who aided in the preparation of this thesis, including Dr. H. L. Mitchell of the Chemistry Department for the use of some equipment, and Mrs. Laurel Ouye of the Botany Department for identifying the microbial cultures.

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SOME OF THE EFFECTS OF NATURAL GAS UPON THE PHYSICAL AND CHEMICAL PROPERTIES OF THE SOIL

by

RUSSELL STANLEY ADAMS, JR.

B. S., Kansas State University, 1958

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agronomy

KANSAS STATE UNIVERSITY
OF AGRICULTURE AND APPLIED SCIENCE

1959

Marked physical, chemical, and biological changes occur in gas-saturated soil. Plant growth may be retarded or eliminated completely. This investigation was conducted to determine the fundamental chemical and physical changes which occur. Emphasis was placed on those factors that might influence plant growth.

Four gas-saturated soils and the adjacent normal soils were studied. For chemical determinations the surface 36 inches of the profile were examined. Total carbon, available phosphorus, soil reaction, exchangeable manganous manganese, exchangeable ferrous iron, and exchangeable ferric iron were determined. Fresh soil samples were analyzed as quickly as possible after sampling for manganous and ferrous ion determinations. Other chemical analyses were made on air-dried soil ground to pass through a 0.2-mm. sieve. The oxidation potentials of these soils were also measured. Physical determinations included water retention, porosity, and bulk density studies at two sites.

Three greenhouse studies were made. Plants were grown on pots of soil transferred from the field; on undisturbed core samples; and on pots watered with water extracts taken from gas-impregnated soils.

In order to determine if gas could be fixed directly to the soil, samples were saturated with gas in the laboratory. These samples were saturated in a series of four treatments. Temperature and length of saturation were varied.

Chemical studies revealed a general increase in total carbon, available phosphorus, and soil reaction in the

gas-saturated soils. The gas-impregnated soils showed a marked increase in manganous manganese and ferric iron. Ferrous iron increased moderately. The oxidation potentials showed the gas-saturated soil to be in a very reduced state.

Water retention and porosity increased in the gas-impregnated soils with a corresponding decrease in bulk density.

Gas-saturated soils produced no injury to plants grown in the greenhouse. Plants watered with water extracts taken from gas-impregnated soils appeared normal.

An increase in carbon was obtained when soil was saturated with natural gas at -1° C. No increase occurred at room temperature. The length of saturation made no difference in the three periods studied. This increase in carbon soon disappeared from the soil when soil was left at room temperature.